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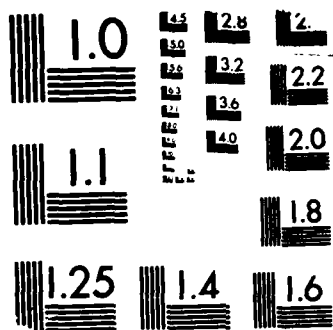   D PHILLIPS DEC 87 DAJA45-87-C-0031

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AD-A193 334

ENERGY MIGRATION, MOTION AND ORDER IN SYNTHETIC POLYMERS

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Report

The initial phase of this work has been concerned exclusively with the luminescence of poly(diacetylenes), so-called one-dimensional polymers.

The chemical structures of some commonly met conjugated polymers are given in Table 1. Of these, PDA's are virtually unique in that they are obtainable as single crystals, and have been selected for study here. The materials studied are the BCMU family, of structure indicated in Table 2.

Figures 1-3 summarise the absorption and emission characteristics of 2,4 and 3-BCMU respectively under various conditions, which are indicated on the diagram captions.

The chromism of BCMU's can be understood in terms of the following forms of the polymer in solution:

Y-form   A coiled structure with a large number of cis double bonds but with some trans still present - Figure 4D.

Y-low T   For 3-BCMU, a slightly wormlike structure (Figure 4C) - for 2 and 4BCMU, a more pronounced wormlike structure.

R form   For 3BCMU, very close to a rigid rod (Figure 4A) - for 2 and 4 BCMU, a slightly wormlike structure which is very like the Y-low T form of 3BCMU.

Glass   Highly ordered rigid rods.

Poly Diacetylenes

In discussing the chromism of PDA's in these terms by comparing figures 1-3, it is important first to note there are fewer fluorescing forms than absorbing ones. This is because the R form consists of long sections of continuously conjugated backbone - be it LCS, wormlike or rigid rods (Figure 4). These forms, as in 'infinitely' conjugated crystals, have a very efficient non-radiative pathway which reduces the quantum yield on transition from Y to R forms. In 4BCMU the red-shifted forms do fluoresce although the quantum yield decreases with decreasing X_c. The presence of an isosbestic point is an important feature of PDA chromism which indicates a phase transition of the polymer without formation of stable, optically detectable, intermediates. For the PDA with sidegroup 9BCMU, a metastable intermediate has been observed. There is a very clear dependence upon the forms of polymer and the sidegroup in the BCMU family. For example, the similarity between results in 2 and 4-BCMU is worthy of comment.

Figure 5 shows that for 3BCMU, a perfectly planar conformation is possible for sections of the backbone, and is stabilised by H-bonding between adjacent sidegroups. A similar picture for 4BCMU can be constructed (Figure 6), and in the perfectly planar case, H-bonding is no longer possible. Twisting of the first few carbon atoms of the sidegroups can allow H-bonding to take place, but at the expense of the planar structure. Similarly 2BCMU has an even number of atoms in its sidegroup, and cannot H-bond in the planar conformation. Thus 2 and 4BCMU have a lower effective conjugation than 3BCMU and are slightly blue-shifted.

The peak in the absorption spectrum depends then, not on the absolute number of carbon atoms in the sidegroup, but on whether that number is even or odd.

If this proposal is correct, then a more pronounced effect would be expected for the red-shifted R forms, which it is proposed consist of rigid rods. This is indeed the case in the Y forms the 'sidegroup shift' is about 10 nm; in the R forms the shift is 110 nm. These effects are best explained by a transition from a coiled structure such as in figure 4D to a planar rigid rod for odd BCMU's and a slightly wormlike structure for even BCMU's. A wormlike to aggregation transition is not consistent with these results.

The transition observed in crystals, or in a solution for a change from Y-low T to R, has been attributed to a butatriene to acetylene isomerisation. However the sidegroup shift in Y-low T forms is only 30 nm, compared to 110 nm in R forms. A change in the resonance structure of the backbone cannot really account for this difference. If the Y form were a coil and the R form a rod, then the Y-low T form (or the metastable intermediate observed in 9BCMU) may be an intermediate form. It may also be due to a conformational transition in the sidegroups themselves, as has been suggested previously by comparison with n-alkane chains and lipid-bilayers.

The idea that the sidegroups themselves are responsible for the transition has been attracting interest recently, both theoretically, and experimentally. A more in-depth study on the sidegroup dependence of transitions in the BCMU family, and other families, will it is hoped permit more vigorous testing of these hypotheses.

In the next phase of this work, in addition to the construction of the evanescent wave fluorimeter, it is intended to return to the study of time-resolved fluorescence of synthetic polymers such as polystyrene and poly (vinyl) naphthalenes in solution.

(2) Papers submitted or published during the period May-December 1987 which acknowledged US Army support:

1. 'Complex decay of fluorescence in synthetic polymers', D.Phillips in 'Photophysics of Polymers' Eds. C.E.Hoyle and J.M.Torkelson. American Chemical Society Symposium Series volume 358, pp. 308-322.

2. 'Time-resolved fluorescence of excimer-forming polymers in solution', D.Phillips, Brit.Polym.J., 1987, 19, 135-149.

3. 'Fluorescence studies of polydiacetylenes in 2-methyl tetrahydrofuran vitreous glasses at low temperatures', S.D.D.V.Rughooputh, D.Bloor, D.Phillips, R.Jankowiak, L.Schutz and H.Bässler, Chem.Phys. (submitted).

(3) During this period, US Army funds were used for the past payment of a replacement laser and ancilliary equipment, for laser dyes, optics and chemicals.

(4) ———

(5) Annex
   (a) Amount of unused funds remaining in contract at end of report $71,278.
   (b) Important property acquired contribution to Coherent 'Antares' mode-locked $Nd^{3+}YAG$:synchronously-pumped dye-laser system.Total value $180,000.

Figure Captions

Figure 1	2BCMU	Y form	$X_c = 1.0$, room temp.
			or Toluene, high temp.
		R form	X_c low, room temp.
			or Toluene, high temp.
		low T	$X_c = 1.0$, room temp.
		Glass	low temp. glass.
Figure 2	4BCMU	Y form	$X_c = 1.0$, room temp.
			or Toluene, high temp.
		R form	X_c low, room temp.
			or Toluene, high temp.
		low T	$X_c = 1.0$, room temp.
		Glass	low temp. glass.
Figure 3	3BCMU	Y form	$X_c = \bar{1}.0$, room temp.
			or Toluene, high temp.
		R form	X_c low, room temp.
			or Toluene, high temp.
		low T	$X_c = 1.0$, room temp.
		Glass	low temp. glass.

Figure 1

Figure 2

POA 4 BCMU

EMISSION (arb. units)

Y-low T

Y

R

Glass

500   600   700nm

POA 4 BCMU

ABSORBANCE (arb units)

Y   lowT   R

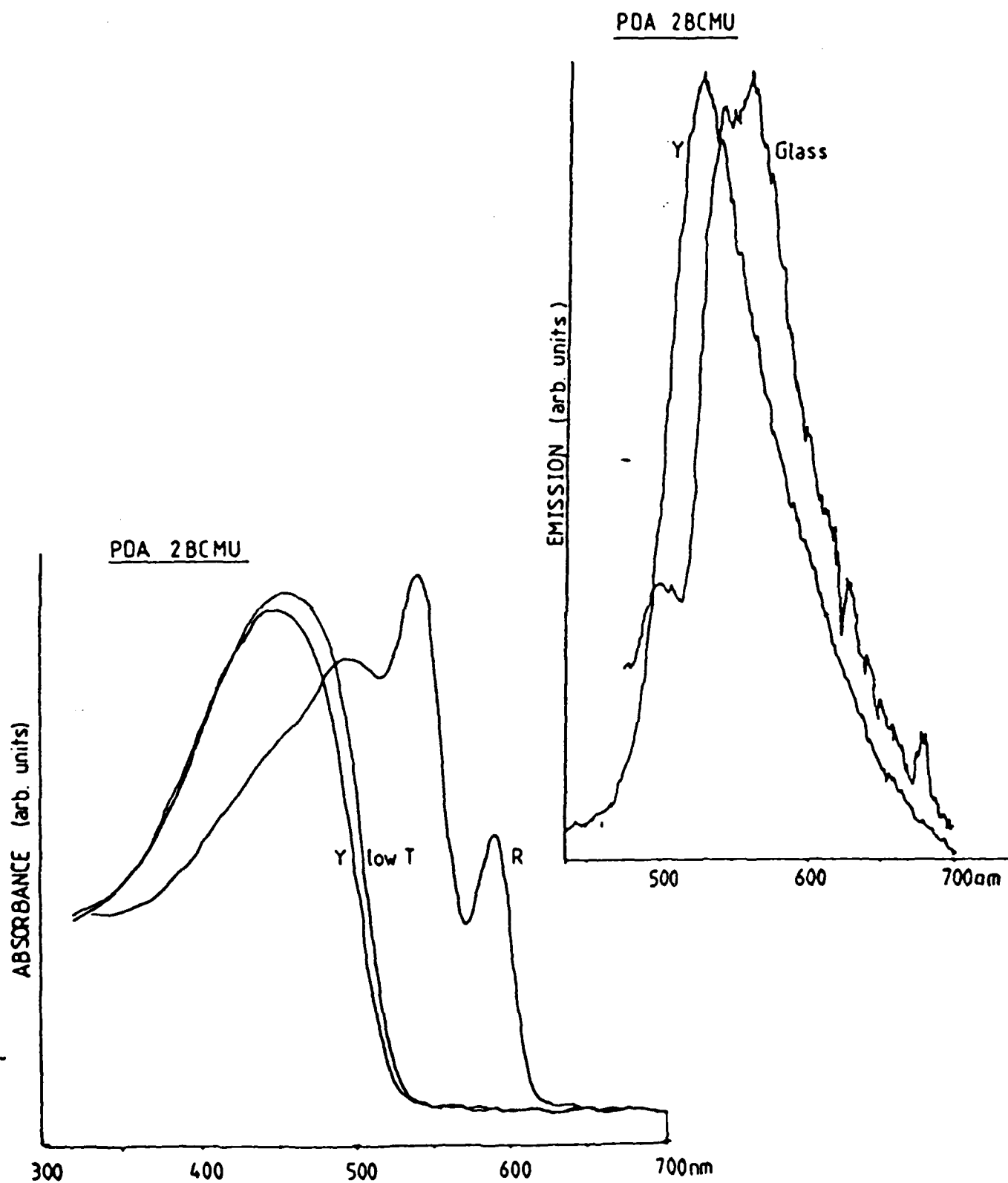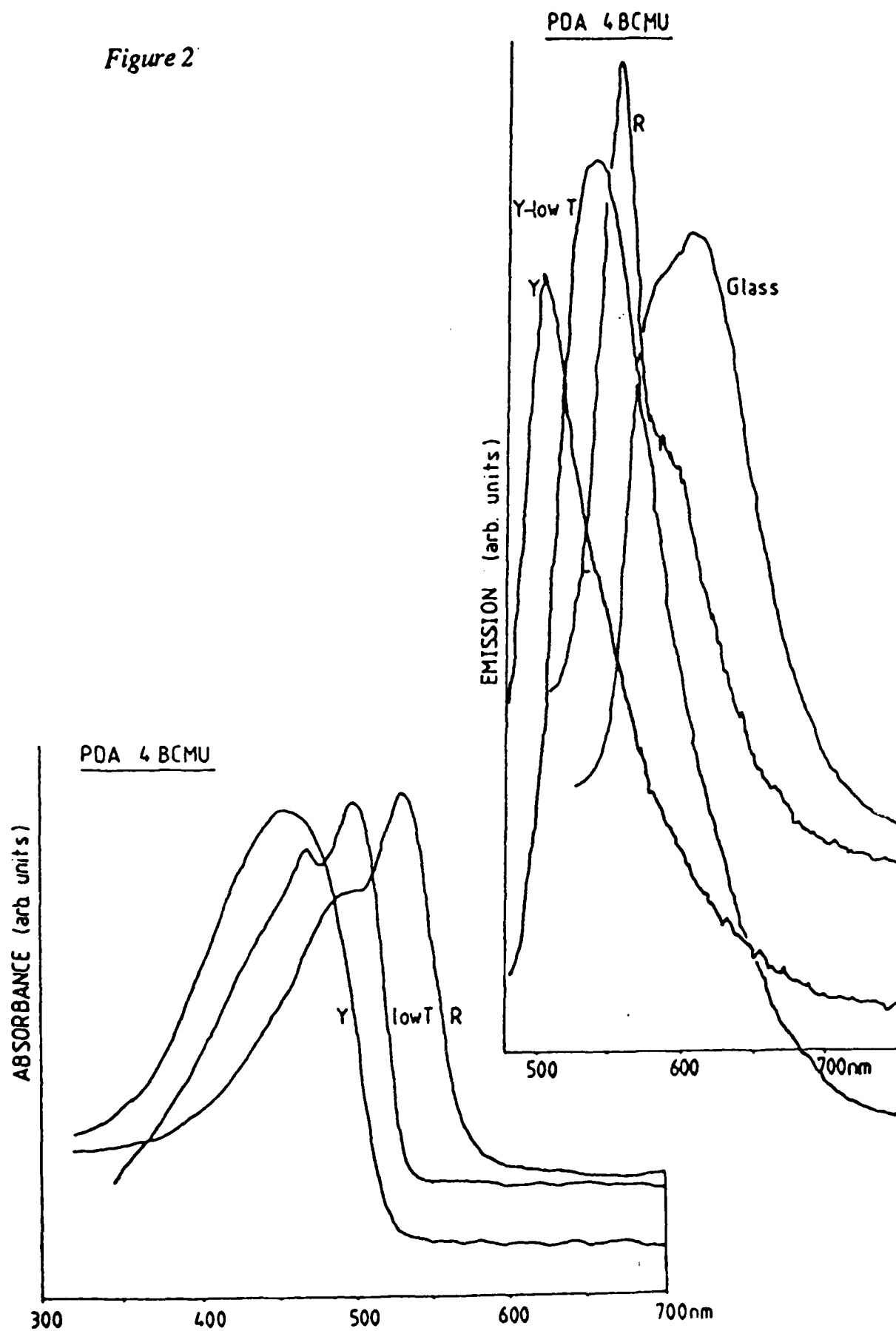300   400   500   600   700nm

Figure 3

Figure 4

A

B
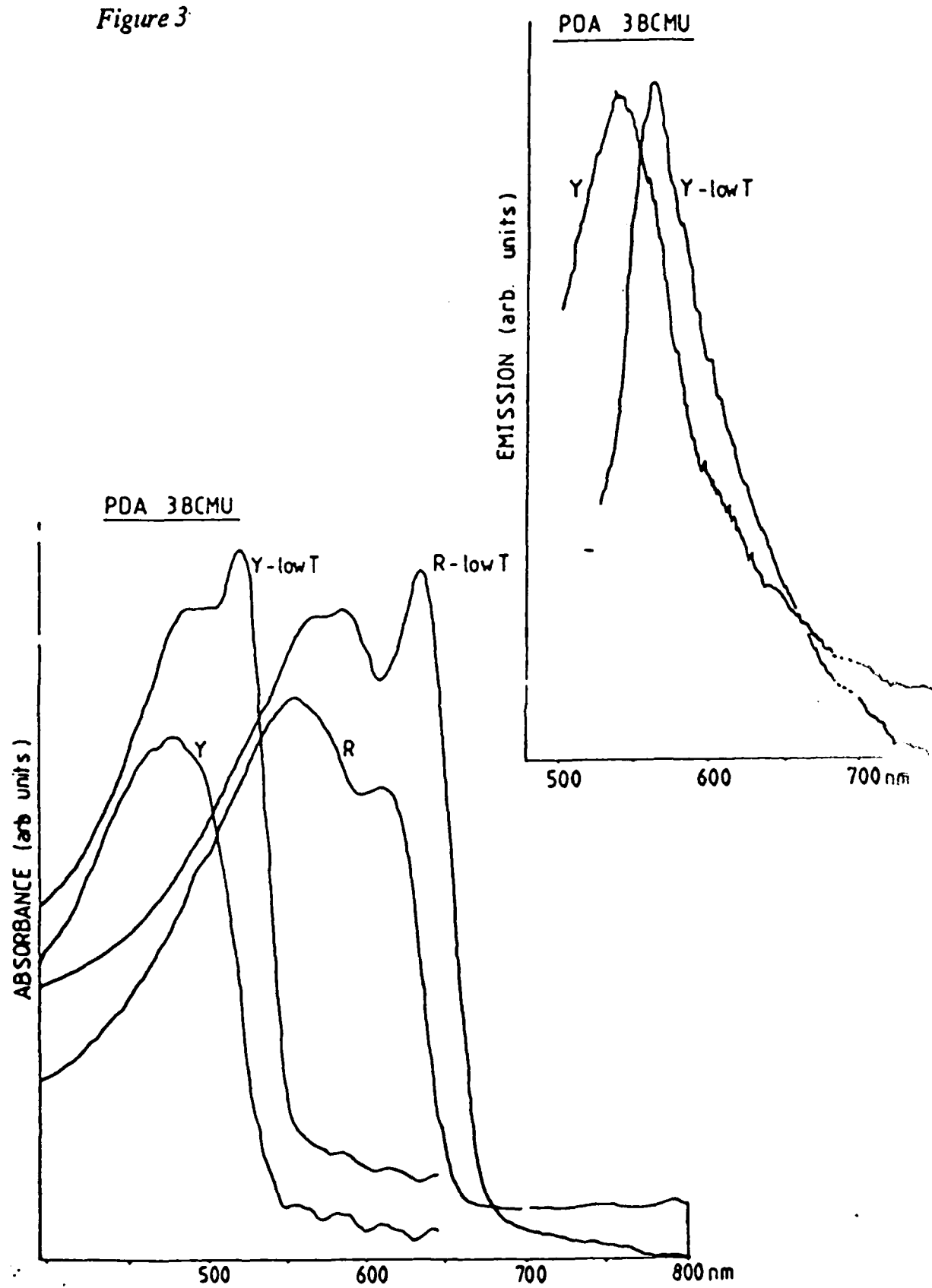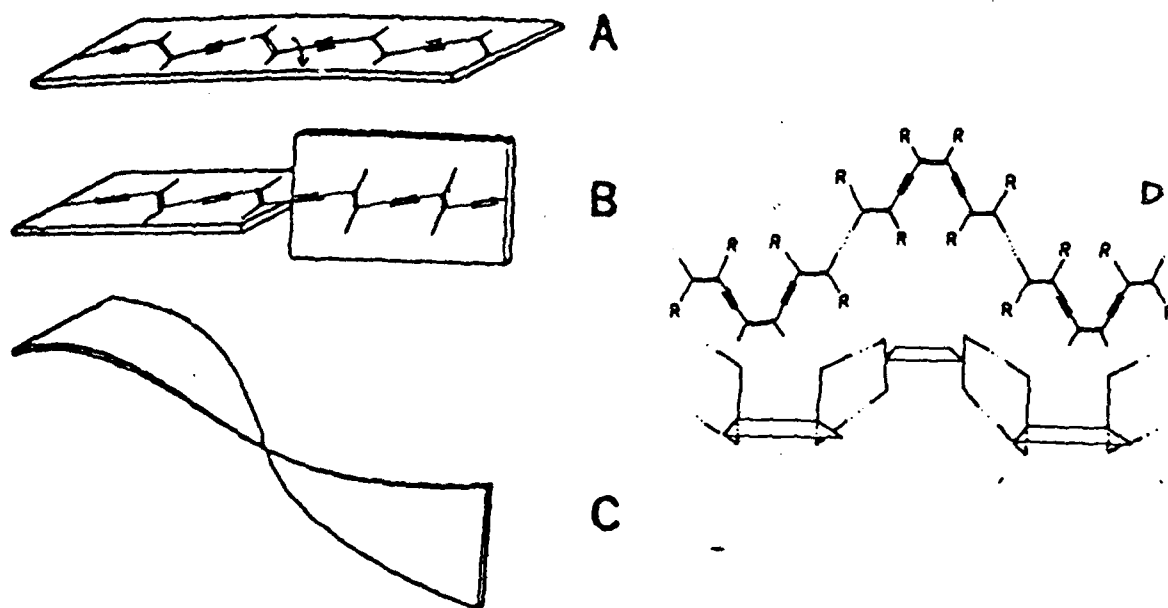
C

D

Figure 5 Planar hydrogen-bonded conformation of poly3BCMU as suggested by molecular models. Hydrogen bonds are indicated by dashed lines.
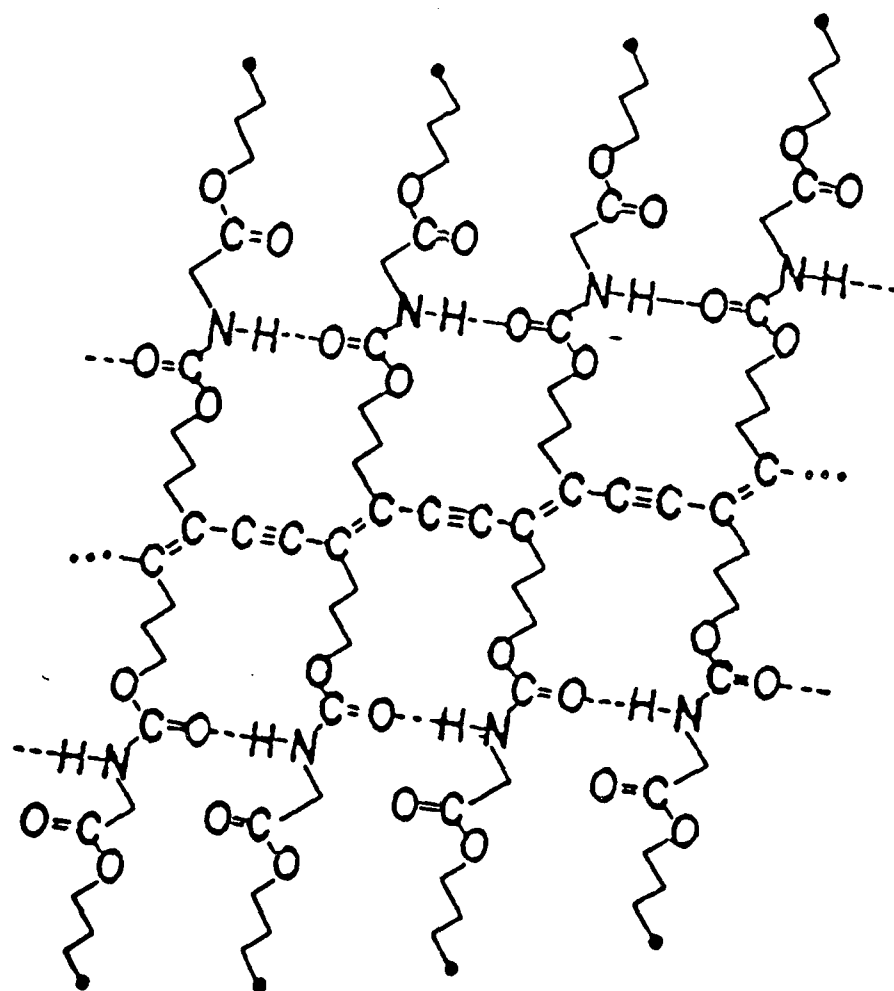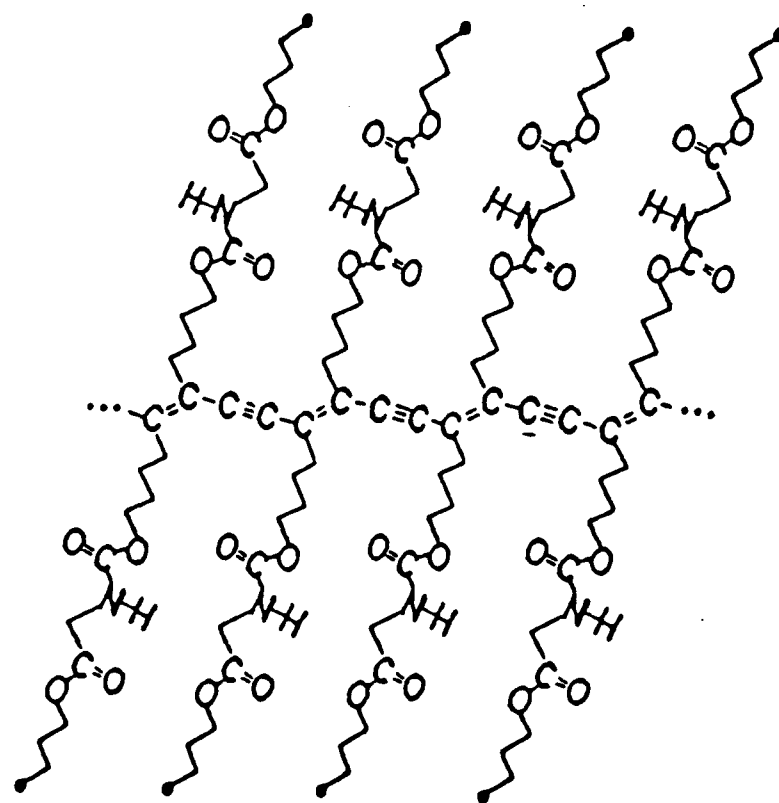
Figure 6

TABLE 1·1

Chemical Structures of some 1D-Conjugated Polymers

QlD Systems	Abbreviation	Structure [†]
Trans-Polyacetylene	trans-PA	$-(CH)_x-$
Cis-Polyacetylene	cis-PA	$-(CH)_x-$
Poly-Phenylene	PPP	[benzene ring structure]$_x$
Poly-Thiopene	PTh	[thiophene ring structure, S]$_x$
Poly-Pyrole	PPy	[pyrrole ring structure, N, H]$_x$
Poly-Aniline	PANI	$-(\phi-N)_x-$
Poly-Phenylene Sulphide	PPPS	$-(\phi-S)_x-$
Poly-Phenylene Vinylene	PPPV	$-(\phi-CH=CH)_x-$
Poly-Phenylene Diphenylvinylene	PDPV	$\left[\phi-\phi-C\!\!\overset{\phi}{=}\!\!\overset{}{\underset{\phi}{C}}\right]_x$
Polydiacetylene	PDA	$=(R'C-C\equiv C-CR)_x=$

[†] ϕ denotes [benzene ring]

Abbrev	Formula	n	forms	solvent
nBCMU	$(CH_2)_n$ OCO NH CH_2 CO C_4H_9	2,3,4,9	sol,film	$CHCl_3$
nECMU	$(CH_2)_n$ OCO NH CH_2 CO C_2H_5	3,4	sol,film	$CHCl_3$
nKAU	$(CH_2)_n$ OCO NH CH_2 CO_2^- K^+	3,4	sol	H_2O
nKA	$(CH_2)_n$ CO_2^- K^+	2,3	sol	H_2O
9PA	$(CH_2)_9$ OCO CH_2 C_6H_5		sol	$CHCl_3$
TS	CH_2 OSO_2 C_6H_4 CH_3		crys sol	$C_6H_5NO_2$
TCDU	$(CH_2)_4$ OCO NH C_6H_5		crys	
1OH	$R'=CH_2OH$ $R=CH_3$		film crys(fibres)	

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